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Origin and degradation of lipids in aeolian particles from a coastal area of the north-western Mediterranean Sea

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ABSTRACT

The lipid content of eight samples of aeolian particles collected on the Frioul Islands (north-western Mediterranean Sea) during the year 2010 was investigated. Lipid analyses indicated a significant contribution of terrestrial higher plant debris to some of the samples, while meat cooking residues were also found. Specific degradation products of sterols and monounsaturated fatty acids were employed to assess the importance of biotic and abiotic degradation processes on land and during aeolian transport. Degradation of higher plant lipids on land appears to involve Type II (i.e., singlet oxygen-mediated) photooxidation during senescence and bacterial degradation processes in soils, while during aeolian transport this terrestrial material mainly undergoes autoxidation and/or Type I (i.e., radical-mediated) photooxidation and is relatively well preserved towards bacterial degradation. In contrast, bacteria play a significant role in the degradation of meat cooking residues in these particles.

1. Introduction

Terrestrially produced particulate organic matter (POM) may be transported relatively quickly through the atmosphere and over long distances and thus influence the organic matter composition of marine sediments, even those far from land (Gagosian et al., 1987; Guerzoni et al., 1999). It is generally considered that this atmospheric transport may be an important way of quickly introducing land-derived OM to the surface of the oceans (Gagosian et al., 1982). Aeolian particles are typically fragments of weathering rocks, soil and biogenic detritus such as terrestrial plant fragments. Other biogenic particles include anthropogenic emissions, bacteria, fungal spores, algae, pollens, seeds and even insects (Simoneit, 2006).

Lipid biomarkers have often been employed to determine the sources of OM in atmospheric particles collected in the open ocean including the Atlantic (Simoneit et al., 1977), Pacific (Gagosian et al., 1982; Kawamura and Gagosian, 1990) and Mediterranean Sea (Sicre et al., 1987). In contrast, there are very few studies dealing with the degradation processes (biotic and/or abiotic) affecting OM in these particles (Stephanou, 1992; Stephanou and Statigakis, 1993). These degradation processes occurring during transport may strongly impact the behaviour of atmospheric OM in the water column (Rontani et al., 2011). To our knowledge, only oxocarboxylic and α,ω-dicarboxylic acids arising from unsaturated fatty acid photooxidation have been detected in aerosols (Sempere and Kawamura, 2003) and proposed as tracers of atmospheric inputs to the sea (Stephanou, 1992; Stephanou and Statigakis, 1993). However, due to the possible formation of these compounds during the senescence of phytoplanktonic cells, this assumption has been challenged by Marchand and Rontani (2001).

The Mediterranean Sea, which is surrounded by many sources of natural and anthropogenic materials, is subject to a continuous input of OM (Guerzoni et al., 1999). In the present paper, we examined the lipid content of aeolian particles collected during 2010 on Frioul Islands (Gulf of Marseille – north-western Mediterranean Sea). Using specific lipid degradation products that have been proposed for distinguishing biotic from abiotic processes, (Rontani et al., 2009, 2011; Christodoulou et al., 2010), we evaluated the roles played by biotic (i.e., heterotrophic), and abiotic (i.e., photodegradative, and autoxidative) processes in the degradation of these particles.

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2. Material and methods

2.1. Sampling collection

The sampling site is located on the Frioul Island (43°15′45″ N 5°17′30″ E), 2 km away from the center of Marseilles (Fig. 1). Atmospheric deposition was collected using an MTX–Italia device which enables us to separate dry from wet deposition. The sample device was a 10 L polyethylene bucket (surface area = 0.063 m^2) placed at around 1.5 m above ground level. Prior to deployment the collector buckets were washed with diluted HCl (10%) and rinsed with ultrapure water. The collectors were generally deployed for one week.

2.2. Sample treatment

At the end of the collection period, each bucket containing dry deposition was brought to the laboratory. 300 ml of ultrapure water were immediately added and the bucket was gently shaken to collect the particulate material stuck to the walls. Then, water containing particulate material was filtered on a pre-weighed glass fiber Whatman filter (47 mm diameter). After filtration the filter was dried at 60 °C and stored dried until analysis. After drying, filters were weighed to determine the mass of particulate matter. Different tests carried out in parallel on wet and dried filters allowed us to demonstrate that autoxidation products of lipid components of aeolian particles were not produced during this drying step.

Lipid biomarkers and their oxidation products were obtained after $NaBH_4$ reduction and subsequent saponification of filters. Reduction of hydroperoxides to alcohols that are amenable to gas chromatography-electron impact mass spectrometry (GC-EIMS) is essential to estimate the importance of photo- and autoxidative degradation processes in natural samples. Indeed, without this preliminary treatment, these labile compounds may be thermally cleaved during alkaline hydrolysis or GC analyses. All manipulations were carried out with foil-covered vessels in order to exclude photochemical artifacts. The preliminary reduction of hydroperoxides ensured that free radical oxidation artifacts were avoided during hot alkaline hydrolysis. The different steps of this treatment ($NaBH_4$-reduction, alkaline hydrolysis, silylation and GC-EIMS analyses) have been previously described (Rontani et al., 2011).

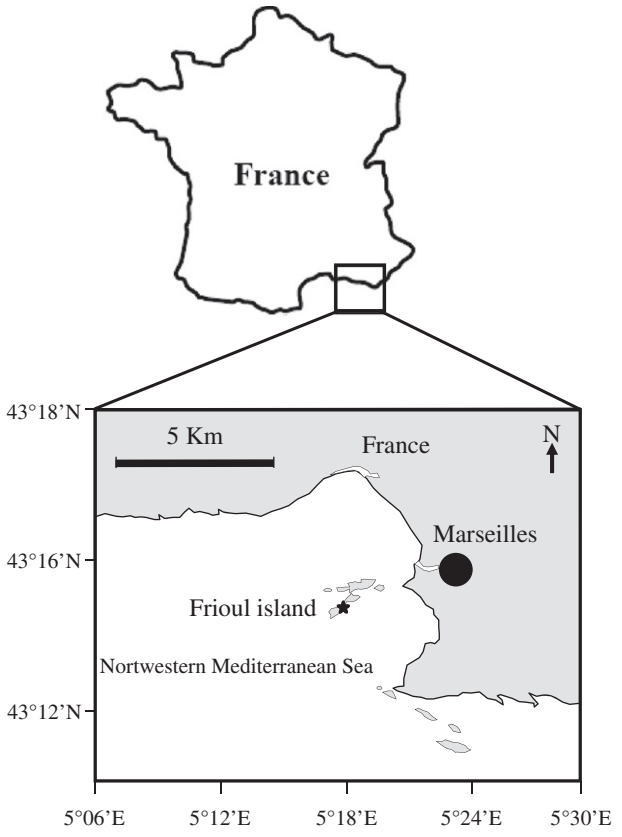

Fig. 1. Map of the studied area with location of the station investigated.

2.3. POC and PON determination

Particulate organic carbon (POC) and particulate organic nitrogen (PON) were determined by using the wet-oxidation procedure of Raimbault et al. (1999).

3. Results and discussion

3.1. Mass fluxes, POC content and C/N ratio

Sample mass fluxes exhibited strong temporal variability with a range of values from 9.1 to 71.1 mg m^{-2} d^{-1} in September and May, respectively (Table 1). These mass fluxes are in the same range than those reported on an annual basis for the western Mediterranean Sea (22 mg m^{-2} d^{-1}, Guerzoni et al., 1999).

C/N ratio is often used as an indicator of the source of OM. Indeed, due to their high protein content, bacteria, algae, yeasts and fungi have relatively low C/N ratios (values ranging from 5 to 10) (Prahl et al., 1980), while terrestrial vascular plants, which mainly consist of cellulose and lignin with low nitrogen content, exhibit C/N ratios of 15 or higher (Hedges et al., 1986). However, this tool must be used with caution because of its variation in the course of OM degradation. Indeed, organic nitrogen is preferentially degraded compared to organic carbon, leading to a C/N increase (Smith et al., 1992), whereas terrestrial organic matter (high C/N ratio) colonization by bacteria (low C:N ratio) may lower the initial terrestrial C/N ratio (Thornton and MacManus, 1994). In the collected samples, C/N ratios exhibited a wide range of values from 8.0 (sample 7S2) to 25.0 (sample 26S2) (Table 1). The lowest values (ranging from 8.0 to 15.5) measured in the samples collected in March and September suggest the presence of relatively fresh nitrogen-rich material. In contrast, the highest values (ranging from 17.1 to 25.0) observed in April, May and July (samples 12S2, 18S2 and 26S2) are indicative of a high degradation state of OM and/or an important contribution of material from terrestrial vascular plants to these samples (Hedges et al., 1986).

Table 1
Sampling period, total mass flux, particulate organic carbon (POC) and nitrogen (PON) fluxes and weight C/N ratio of the aeolian particles.

Code[a]	Sampling period	Mass flux (mg m^{-2} d^{-1})	POC flux (mg m^{-2} d^{-1})	PON flux (mg m^{-2} d^{-1})	C/N (wt)
7S2	25 February–03 March 2010	31.6	1.51	0.19	8.0
8S2	03–10 March 2010	27.7	2.17	0.14	15.5
9S2	10–16 March 2010	21.2	1.75	0.12	14.6
10S2	16–24 March 2010	29.1	1.55	0.18	8.6
12S2	31 March–09 April 2010	30.6	3.25	0.19	17.1
18S2	12–19 May 2010	71.1	8.13	0.41	19.8
26S2	08–15 July 2010	16.7	2.75	0.11	25.0
36S2	16–23 September 2010	9.1	2.54	0.20	12.7

[a] In the code the first number indicates the week of sampling.

3.2. Contribution of lipid organic carbon to the POC

POC in the different samples (Table 1) was compared to the quantity of carbon found in the lipids which could be extracted and quantified. The results obtained are summarized in Fig. 2. The percentage of extracted lipids, which are strongly dominated by fatty acids, appears to range from 8 to 38% of POC. It may be noted that very similar values were previously observed by Gröllert and Puxbaum (2000) in aerosols from alpine sites. The large fraction of POC still remaining but not extractable is likely to consist of recalcitrant highly polar or macromolecular structures such as lignin, cellulose and humic acids. Interestingly, the lowest percentage of extracted lipids was observed in the case of the 26S2 sample exhibiting the highest C/N ratio (Table 1) and thus expected to contain the more degraded OM.

3.3. Quantification of classical lipid biomarkers in the different aeolian particle samples

3.3.1. Sterols and n-alkanols

Sterols are among the most specific and diverse lipid biomarkers that can trace the contribution from algae, higher animals, vascular plants and sewage contamination (Volkman, 1986). This, coupled with the relatively high resistance of the sterol skeleton to extensive degradation after release into the environment, makes them valuable as biomarkers.

Sterols measured in the different aeolian particle samples exhibited a predominance of 24-ethylcholest-5-en-3β-ol (sitosterol) or cholest-5-en-3β-ol (cholesterol) (Table 2). Their flux ranges were 1–100 μg m^{-2} d^{-1} and 2–14 μg m^{-2} d^{-1}, respectively. Sitosterol is present in some marine algae (Volkman, 1986), but it also constitutes the major sterol of vascular plants. Thus, the occurrence of sitosterol in aeolian particles generally indicates the presence of plant-derived material. In contrast, cholesterol has been proposed as one of the molecular tracers for assessing emissions from meat cooking in urban zones. Indeed, this sterol in beef is emitted directly without molecular alteration into smoke during grilling and frying (Simoneit et al., 1993). Cholesterol may also arise from algae and zooplankton (Volkman, 1986). If the lack of 24-methylcholesta-5,22*E*-dien-3β-ol and 24-methylcholesta-5,24(28)-dien-3β-ol in the samples does not support an algal origin, a contribution of zooplankton to this sterol (although unlikely due to the short distances over the sea before reaching the island sampling station) cannot be totally excluded. We failed to detect 24-methylcholesta-5,7,22*E*-trien-3β-ol (ergosterol), which is a typical sterol of yeasts and fungi (Weete et al., 2010). The results obtained (Table 2) indicate the presence of higher plant debris in the different samples examined, this contribution being highest in the samples 7S2, 8S2, 12S2 and 18S2. The highest C/N ratio observed in the case of the sample 26S2 (Table 1) seems thus to result from a high degradation state of OM rather than from an important contribution from terrestrial vascular plants. Further analyses of lipid degradation products allowed to confirm this assumption (see section 3.4). Cholesterol probably arising from meat cooking residues appears to mainly contribute to the samples 9S2, 10S2, 26S2 and 36S2 (Table 2).

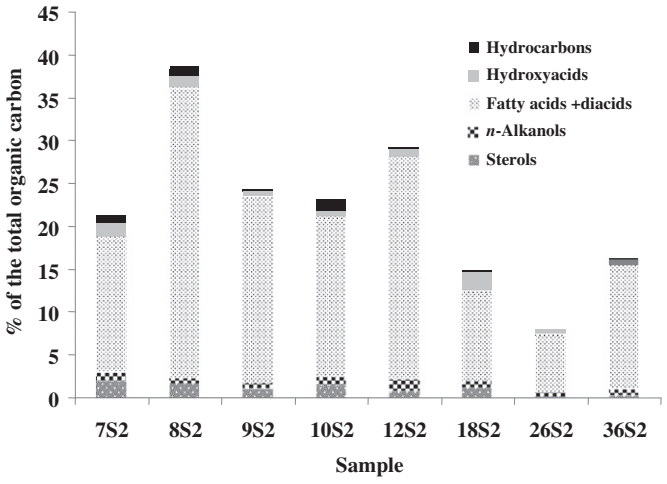

Fig. 2. Contribution of lipid organic carbon to the TOC.

The samples also contain low amounts of *n*-alkanols. Their distributions are characterized by a strong even-carbon number predominance (Table 2). The dominance of C_{24} and C_{26} homologues in the samples 12S2 and 18S2 indicates a strongest contribution of higher plant debris to these samples (Kolattukudy, 1976). These observations are well correlated with the dominance of sitosterol in the sample 18S2 and to a lesser extent in the sample 12S2 (Table 2), but a lack of correlation was observed in the case of the samples 7S2 and 8S2 also containing a high proportion of sitosterol. These differences could be attributed to the relative lability of *n*-alkanols. Indeed, in contrast to sterols, these compounds may be easily metabolized by bacteria (via the corresponding fatty acids), this lability limiting their use as biomarkers. A contribution of wind-blown diatoms containing sitosterol to the samples 7S2 and 8S2 could be another possible explanation. Indeed, Seyve and Fourtanier (1985) previously detected diatoms in Saharan dusts collected in southern France. Interestingly, the diatom flora of these dusts is generally dominated by *Aulacoseira* species (Harper and MacKay, 2010), whose major sterols are cholesterol, campesterol and sitosterol (Rampen, 2009). A significant contribution of wind-blown freshwater diatoms to sample 7S2 is well supported by: (i) its relatively low C/N ratio (Table 1) close to that of algae (Prahl et al., 1980) and (ii) the strong influence of south-east wind on the air masses associated with this sample (Fig. 3).

3.3.2. Fatty acids

Homologous series of saturated linear fatty acids (C_{10}–C_{28}) have been detected in the different samples investigated (Table 3). C_{16} and C_{18} appeared to be the most abundant homologues (fluxes ranging from 110 to 770 μg m^{-2} d^{-1} and from 84 to 594 μg m^{-2} d^{-1}, respectively). These non-specific fatty acids are derived from several sources including algae, bacteria, fungi, yeasts, animals and terrestrial higher plants (Simoneit, 2006; Harwood and Russell, 1984; Kawamura et al., 2003). In contrast, long-chain (C_{20}–C_{28}) fatty acids, which are characteristic of epicuticular waxes of higher plants (Kolattukudy, 1976; Gagosian et al., 1987), were only present in very low proportions in the different samples examined (Table 3). Fatty acids are generally much more susceptible to microbial degradation than other lipids (Wakeham, 1995). Intense and selective bacterial degradation in soils or during the early stages of atmospheric transport could thus explain the very weak amounts of these higher plant tracers observed in the samples 12S2 and 18S2 containing high proportions of sitosterol (Table 2) and exhibiting a high C/N ratio (Table 1). This hypothesis is well supported by: (i) the lack of isoprenoid compounds deriving from the phytyl side-chain of chlorophyll (generally considered as more resistant towards bacterial degradation than fatty acids) and (ii) the presence of relatively high proportions of $C_{18:1\omega7}$ fatty acid (vaccenic acid) (a typical bacterial biomarker, Sicre et al., 1988) in these samples (ratio $C_{18:1\omega7}/C_{16:0}$ ranging from 0.14 to 0.37) (Table 3).

Significant contributions (flux ranging from 13 to 451 μg m^{-2} d^{-1}) of the non-specific $C_{18:1\omega9}$ fatty acid (oleic acid) originating from higher plants, fungi, yeasts, bacteria, animals or

Table 2
Flux of *n*-alkanols and sterols in the different samples.

Compound	Flux (μg m^{-2} d^{-1})							
	Sample 7S2	Sample 8S2	Sample 9S2	Sample 10S2	Sample 12S2	Sample 18S2	Sample 26S2	Sample 36S2
$C_{14:0}$ alkan-1-ol	0.2	0.3	tr	0.2	3.0	3.2	0.5	0.9
$C_{15:0}$ alkan-1-ol	tr[a]	tr	tr	tr	tr	tr	0.2	0.3
$C_{16:0}$ alkan-1-ol	1.7	2.5	1.1	2.2	9.0	9.8	4.0	3.7
$C_{17:0}$ alkan-1-ol	tr	tr	tr	tr	0.6	tr	0.4	0.4
$C_{18:0}$ alkan-1-ol	3.8	4.1	2.4	4.1	9.4	10.3	6.1	6.6
$C_{19:0}$ alkan-1-ol	tr	tr	tr	tr	tr	tr	tr	tr
$C_{20:0}$ alkan-1-ol	3.8	3.7	2.5	7.2	10.8	11.8	2.3	2.6
$C_{21:0}$ alkan-1-ol	tr	tr	tr	tr	tr	tr	tr	0.3
$C_{22:0}$ alkan-1-ol	4.3	4.6	3.2	6.5	6.3	6.8	1.9	3.3
$C_{23:0}$ alkan-1-ol	tr	tr	tr	tr	tr	tr	0.2	tr
$C_{24:0}$ alkan-1-ol	1.3	2.3	1.1	0.7	17.9	19.5	1.0	1.1
$C_{25:0}$ alkan-1-ol	tr	tr	tr	tr	tr	tr	0.2	0.2
$C_{26:0}$ alkan-1-ol	1.2	tr	tr	tr	15.2	16.5	1.2	0.9
$C_{27:0}$ alkan-1-ol	tr	tr	tr	tr	tr	tr	tr	tr
$C_{28:0}$ alkan-1-ol	tr	tr	tr	tr	2.5	2.8	0.4	0.3
$C_{29:0}$ alkan-1-ol	tr	tr	tr	tr	tr	tr	tr	tr
$C_{30:0}$ alkan-1-ol	tr	tr	tr	tr	tr	tr	tr	tr
Cholest-5-en-3β-ol	4.8 (21)[b]	7.6 (16)	6.7 (33)	14.1 (43)	9.6 (24)	8.5 (7)	1.7 (50)	4.0 (42)
24-Methylcholest-5-en-3β-ol	3.0 (13)	4.8 (10)	3.0 (14)	3.3 (10)	6.2 (15)	14.4 (11)	0.2 (6)	0.5 (6)
24-Ethylcholesta-5,22-dien-3β-ol	2.0 (8)	6.2 (13)	1.7 (9)	2.3 (7)	0.8 (2)	3.1 (3)	0.2 (6)	0.9 (10)
24-Ethylcholest-5-en-3β-ol	13.5 (58)	29.5 (61)	9.3 (44)	13.0 (40)	23.8 (59)	99.6 (79)	1.3 (38)	4.0 (42)

[a] Trace amounts (flux < 0.2 μg m^{-2}).
[b] Relative percentages of sterols.

algae (Harwood and Russell, 1984) were also detected in the different samples (Table 3).

3.3.3. Hydrocarbons

The flux of total *n*-alkanes (C_{21}–C_{34}) ranged from 2 to 33 μg m^{-2} d^{-1} (Table 4). The CPI (Carbon Preference Index, concentration ratios of odd-carbon *n*-alkanes over even-carbon *n*-alkanes) are given in Table 4. Hydrocarbons originating from land plant material show a predominance of odd-numbered carbon chains with CPI values ranging from 5 to 10 (Hedges and Prahl, 1993), whereas petrogenic hydrocarbons have a CPI approximating 1.0 (Farrington and Tripp, 1977). CPI values close to 1.0 also are thought to indicate greater input from marine microorganisms and/or recycled organic matter (Kennicutt et al., 1987).

Relatively strong odd-to even predominance (CPI ranging from 5.1 to 7.8) (Table 4), attesting to a predominant contribution from higher plants to *n*-alkanes, was observed for samples 12S2, 18S2, 26S2 and 36S2 collected between April and September. In contrast, the moderate odd-carbon predominance observed in the other samples collected in February–March (CPI ranging from 1.2 to 2.7) (Table 4) suggests that both biogenic and petrogenic hydrocarbon sources contributed to them. It may be noted that the relatively weak values of CPI observed in samples 7S2 and 8S2 well support the expected contribution of diatoms to these samples (see section 3.3.1).

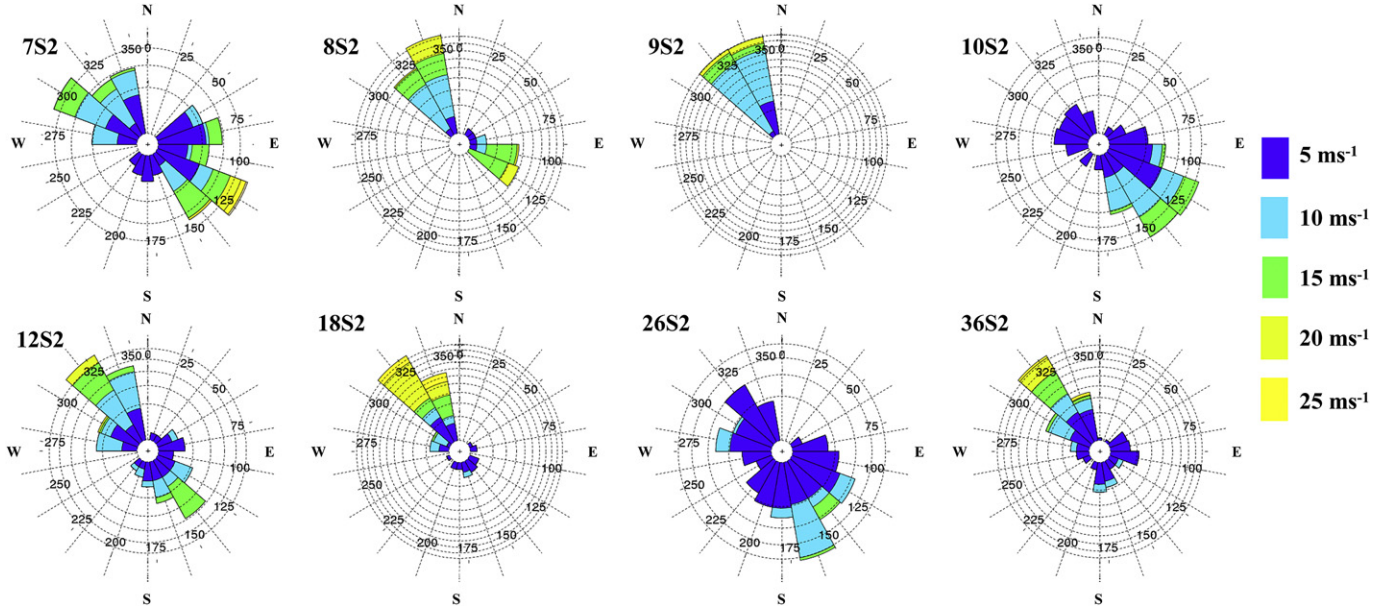

Fig. 3. Rosewind for the eight samples investigated.

Table 3
Flux of fatty acids and diacids in the different samples.

Compound	Flux ($\mu g\ m^{-2}\ d^{-1}$)							
	Sample 7S2	Sample 8S2	Sample 9S2	Sample 10S2	Sample 12S2	Sample 18S2	Sample 26S2	Sample 36S2
$C_{10:0}$ FA	0.3	1.0	1.0	0.6	0.5	0.6	0.3	0.2
$C_{11:0}$ FA	0.1	0.1	0.2	0.1	1.2	0.5	tr	0.1
$C_{12:0}$ FA	0.3	0.8	1.3	0.4	0.8	2.8	0.7	0.9
$C_{13:0}$ FA	0.1	0.2	0.3	0.1	0.8	0.7	0.2	0.1
$C_{14:0}$ FA	5.5	16.0	9.2	6.7	28.7	26.3	7.4	107.5
$C_{15:0}$ FA *iso*	0.8	1.4	0.4	1.1	4.3	5.2	0.6	0.9
$C_{15:0}$ FA *anteiso*	1.2	2.1	0.8	1.8	9.3	4.6	1.1	1.5
$C_{15:0}$ FA	4.1	7.2	5.2	5.7	13.8	23.5	3.8	5.3
$C_{16:1}$ FA	5.9	16.4	7.0	7.1	16.0	50.5	4.8	8.3
$C_{16:0}$ FA	108.9	347.4	152.1	159.3	770.8	603.1	111.2	142.5
$C_{17:0}$ FA branched	2.9	4.9	1.7	3.5	5.5	6.6	2.1	3.2
$C_{17:1}$ FA	1.4	1.4	0.3	1.8	8.5	7.6	1.1	3.8
$C_{17:0}$ FA	3.2	8.7	4.1	5.1	6.2	12.0	2.5	4.7
$C_{18:1\ \omega9}$ FA	27.4	42.6	13.4	28.7	450.6	111.4	33.3	22.2
$C_{18:1\ \omega7}$ FA	9.3	10.5	3.7	14.6	62.2	43.9	21.5	11.7
$C_{18:0}$ FA	132.9	594.3	327.5	221.6	166.9	316.4	84.4	236.9
$C_{19:0}$ FA	0.6	0.1	0.4	0.6	tr	1.0	tr	0.8
$C_{20:0}$ FA	4.3	11.2	5.3	5.1	19.8	24.4	4.4	6.8
$C_{21:0}$ FA	0.1	tr	tr	tr	tr	1.3	tr	0.2
$C_{22:0}$ FA	2.5	4.5	1.3	1.4	2.3	23.1	1.7	2.2
$C_{23:0}$ FA	0.2	tr	tr	tr	tr	1.1	tr	0.1
$C_{24:0}$ FA	0.8	1.1	1.3	0.3	1.4	11.1	0.7	1.0
$C_{25:0}$ FA	tr[a]	tr	tr	tr	tr	1.3	tr	tr
$C_{26:0}$ FA	0.1	tr	0.5	tr	tr	2.2	0.1	tr
Ratio $C_{18:1\omega7}/C_{16:0}$	0.069	0.017	0.011	0.066	0.370	0.139	0.272	0.051
$C_{8:0}$ diacid	0.1	tr	tr	0.1	2.0	1.3	0.2	0.2
$C_{9:0}$ diacid	0.6	0.7	tr	0.8	21.7	11.2	1.7	1.1
$C_{10:0}$ diacid	0.2	tr	tr	0.3	1.4	1.5	0.5	0.3
$C_{11:0}$ diacid	0.3	tr	tr	0.4	0.8	1.0	0.6	0.2

[a] Trace amounts (flux $< 0.1\ \mu g\ m^{-2}\ d^{-1}$).

3.3.4. Hydroxyacids

β- and ω-Hydroxyacids ranging from C_{10} to C_{14} and from C_8 to C_{17}, respectively, were detected in the different samples (Table 5). These compounds are well-known intermediates in oxidative biotransformation of fatty acids. β-Oxidation, which is the more widely distributed degradation pathway of fatty acids in microorganisms (Lehninger, 1975), may account for the formation of the β-hydroxyacids detected. ω-Hydroxyacids can be produced by terminal oxidation of fatty acids by microorganisms (Miura and Fulco, 1975). However, the shorter homologues (C_8–C_{11}, C_9 being the most abundant) could also result from $NaBH_4$-reduction of the corresponding ω-oxocarboxylic acids arising from the cleavage of photo- or autoxidation products (allylic hydroperoxides) of Δ^9-unsaturated fatty acids (see section 3.4.2). The presence of the highest amount of C_9 ω hydroxyacid in the 12S2 sample (Table 5) containing the highest proportion of oleic acid oxidation products (Table 6) well supports such an origin.

Cutin is present in the cuticle (the outer layer of the epidermal cells of primary plant tissues, such as leaves), it is known to be an insoluble polyester polymer whose depolymerisation during alkaline hydrolysis affords several monomers and notably ω-hydroxyhexadecanoic acid and isomeric C_{16} dihydroxycarboxylic acids (Holloway and Brown-Deas, 1973). The detection of a high proportion of these compounds in the sample 18S2 and to a lesser extent in the sample 12S2 (Table 5) confirms the strong contribution of higher plants to these samples.

3.4. Analyses of lipid oxidation products

To evaluate potential effects of abiotic degradation, we measured a suite of lipid oxidation products as tracers of both biotic and abiotic processes (Christodoulou et al., 2009; Rontani et al., 2009, 2011). These tracers convey two important pieces of information. First, they help discern the mechanisms of degradation, whether biological or abiological, and if the later, whether photooxidative or autoxidative. Second, they may provide some information on the source of the OM that is subject to the different degradation processes.

3.4.1. Chlorophyll

We failed to detect the chlorophyll phytyl side-chain in the different samples. Chlorophyll of higher plants debris seems thus to have been totally degraded in soils. A degradation during the early stages of atmospheric transport cannot be totally excluded, but due to the relative recalcitrance of isoprenoid compounds towards biodegradation processes, it seems unlikely. It was previously demonstrated that Type II photooxidation processes (i.e., involving singlet oxygen) act intensively on chlorophyll phytyl side-chain during the senescence of higher plants (Rontani et al., 1996). The lack of classical photooxidation products of phytol in these samples results probably from the involvement of intensive bacterial degradation in soils.

Table 4
Flux of *n*-alkanes and Carbone Preference Index (CPI) in the different samples.

Sample	Flux ($\mu g\ m^{-2}\ d^{-1}$)	CPI
7S2	14.1	2.4
8S2	32.9	2.6
9S2	4.4	2.7
10S2	29.3	1.2
12S2	5.7	7.1
18S2	22.6	5.9
26S2	2.0	4.1
36S2	1.6	6.0

Table 5
Flux of hydroxyacids in the different samples.

Compound	Flux (μg m^{-2} d^{-1})							
	Sample 7S2	Sample 8S2	Sample 9S2	Sample 10S2	Sample 12S2	Sample 18S2	Sample 26S2	Sample 36S2
$C_{8:0}$ ω hydroxyacid	tr[a]	tr	tr	tr	3.2	0.2	tr	tr
$C_{9:0}$ ω hydroxyacid	tr	tr	tr	tr	18.3	1.9	0.2	0.4
$C_{10:0}$ ω hydroxyacid	tr	tr	tr	2.1	2.2	1.1	0.3	0.3
$C_{11:0}$ ω hydroxyacid	tr	tr	tr	0.8	1.8	0.6	1.1	2.1
$C_{12:0}$ ω hydroxyacid	9.6	16.0	3.3	6.3	7.9	33.7	3.1	5.9
$C_{14:0}$ ω hydroxyacid	3.1	4.7	0.9	1.8	tr	9.9	0.9	1.7
$C_{16:0}$ ω hydroxyacid	7.0	10.2	3.2	5.6	2.7	48.5	9.9	3.7
$C_{17:0}$ ω hydroxyacid	0.9	tr	tr	tr	tr	14.4	0.8	tr
$C_{10:0}$ β hydroxyacid	tr	tr	tr	tr	3.8	1.4	tr	tr
$C_{12:0}$ β hydroxyacid	0.4	tr	tr	0.7	5.5	2.2	0.4	0.5
$C_{14:0}$ β hydroxyacid	1.4	0.7	0.5	2.5	11.2	5.6	0.3	1.5
$C_{16:0}$ β hydroxyacid	1.1	tr	0.5	2.0	0.8	4.2	0.4	2.8
$C_{18:0}$ β hydroxyacid	0.4	tr	tr	0.7	tr	2.9	tr	tr
Isomeric C_{16} dihydroxyacids[b]	15.7	20	4.2	3.7	22.5	187.1	11.5	9.2
Isomeric C_{16} hydroxydiacids[c]	0.4	tr	tr	tr	tr	9.2	0.4	tr

[a] Trace amounts (flux < 0.2 μg m^{-2} d^{-1}).
[b] Mixture of 8,18-, 9,18- and 10,18-dihydroxyhexadecanoic acids.
[c] Mixture of 8-, 9- and 10-hydroxyhexadecanedioic acids.

3.4.2. Unsaturated fatty acids

The reactivity of unsaturated fatty acids relative to auto- and photooxidative processes logically increases with the number of double bonds (Frankel, 1998). Although oxidation products of polyunsaturated acids (PUFA) are thus considered to be very sensitive tracers of these processes, they are not stable enough to be used for this purpose. In contrast, autoxidation and photooxidation of monounsaturated fatty acids lead to the formation of oxidation products stable enough in the environment to act as markers of these processes (Marchand and Rontani, 2001; Marchand et al., 2005).

Autoxidation and type I (i.e., involving hydrogen abstraction) photosensitized oxidation of oleic acid affords a mixture of six *Z* and *E* isomeric allylic hydroperoxyacids: 8-*E*, 8-*Z*, 9-*E*, 10-*E*, 11-*E* and 11-*Z* hydroperoxides (Frankel, 1998) (Fig. 4). In contrast, type II (i.e., singlet oxygen-mediated) photooxidation of this compound produces a mixture of 9- and 10-hydroperoxides with an allylic *E*-double bond (Frankel, 1998), which can undergo highly stereoselective radical allylic rearrangement respectively to 11-*E* and 8-*E* hydroperoxides (Porter et al., 1995). Given that the *Z* configurations are specific to free radical processes, the relative importance of type II and free radical processes can easily be distinguished by quantifying these compounds (in the form of the corresponding alcohols) after $NaBH_4$-reduction (Marchand and Rontani, 2001).

Table 6
Percentages (relative to the residual parent compound) of degradation products of oleic acid in the different samples.

Sample	Allylic hydroxyacids[a] (%)	9-10-Epoxyoctadecanoic acid[b] (%)	Total (%)
7S2	49.1	47.7	96.8
8S2	49.6	–	49.6
9S2	12.6	–	12.6
10S2	37.9	15.9	53.8
12S2	119.4	79.4	198.8
18S2	87.0	137.4	224.4
26S2	79.6	188.0	267.6
36S2	17.6	6.5	22.1

[a] Mixtures of 9-hydroxyoctadec-10(*trans*)-enoic, 10-hydroxyoctadec-8(*trans*)-enoic, 8-hydroxyoctadec-9(*cis* and *trans*)-enoic and 11-hydroxyoctadec-9(*cis* and *trans*)-enoic acids.
[b] Quantified under the form of the corresponding methoxyhydrins, diols and chlorohydrins after the treatment.

Fatty acids and their oxidation products may be easily metabolized by bacteria (Marchand et al., 2005); in the present case this lability may be very useful for understanding the abiotic degradation processes acting in aeolian particles. Indeed, fatty acid oxidation products produced during the senescence of terrestrial higher plants should be totally degraded before they have an opportunity to contribute to aeolian particles and we can thus assume that the information conveyed by these tracers is indicative of the degradation acting during atmospheric transport. This hypothesis is well supported by the lack of isoprenoid compounds deriving from the photodegradation of chlorophyll phytyl side-chain of higher plants (more resistant towards bacterial degradation than fatty acids) in the samples analyzed. Because oleic acid has diverse biological sources, we used abundances of its oxidation products to assess abiotic degradation of the bulk OM of particles. The profiles obtained (Fig. 5) exhibited very strong proportions of *Z* configurations, which attest to the practically exclusive involvement of autoxidative or type I photosensitized oxidative processes in the different samples and to the complete degradation of Type II photooxidation products produced during the senescence of terrestrial higher plants. Due to the lack of adequate sensitizers (e.g., chlorophyll), type II photoprocesses appear to act very weakly in aeolian particles. For a quantitative point of view, it may be noted that the percentage of allylic hydroxyacids relative to the residual parent oleic acid ranged from 13 to 120% (Table 6). The highest oxidation states were logically observed during the spring and summer periods (samples 12S2, 18S2 and 26S2), when the temperature and light intensity favour autoxidation and type I photosensitized processes.

Allylic hydroperoxides thus formed may undergo: (i) heterolytic cleavage catalyzed by protons (Frimer, 1979) and (ii) homolytic cleavage induced by transition metal ions (Schaich, 2005) or UVR (Christodoulou et al., 2010). Proton-catalysed cleavage of allylic hydroperoxides involves mainly the migration of the vinyl group (Frimer, 1979) (Fig. 6). According to this pathway, allylic hydroperoxides resulting from the light-induced oxidation of unsaturated fatty acids can afford ω-oxocarboxylic acids and aldehydes (Fig. 6). In the presence of peroxides or molecular oxygen such compounds can then be easily oxidized respectively to carboxylic and α,ω-dicarboxylic acids. Heterolytic cleavage of the isomeric allylic hydroperoxides identified thus provides an explanation for the formation of the C_8–C_{11} α,ω-dicarboxylic acids detected

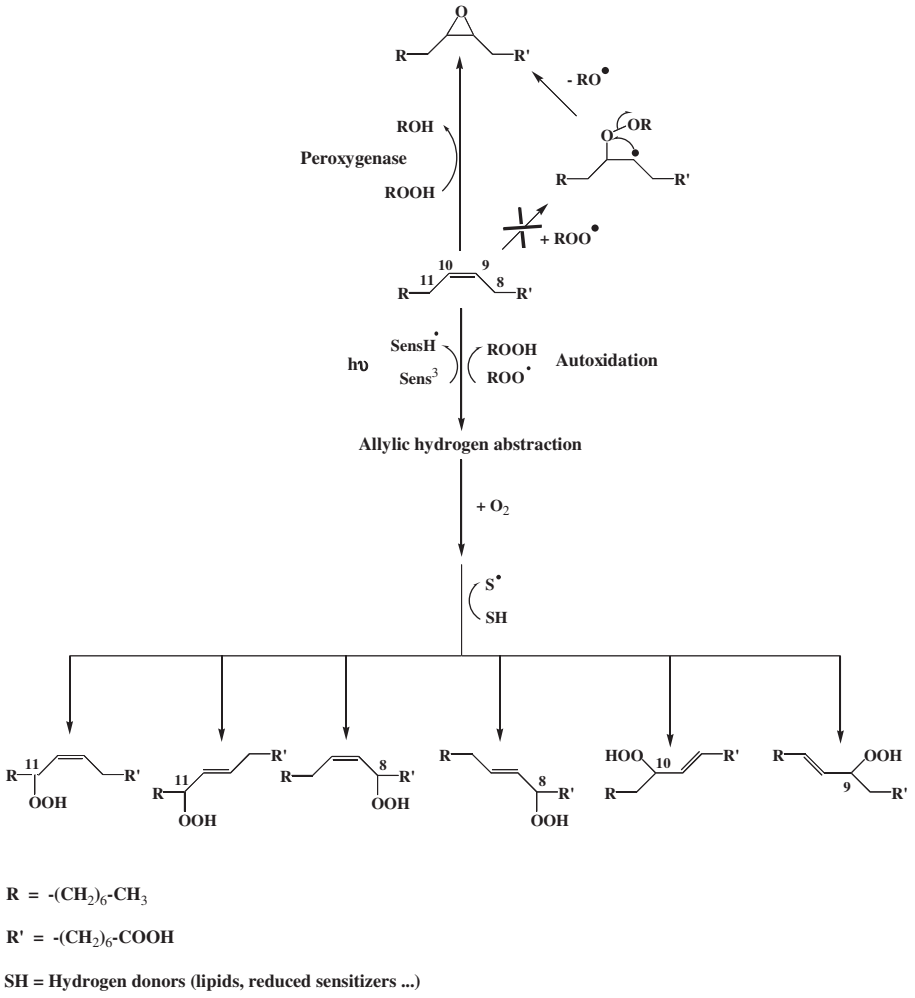

Fig. 4. Degradation products resulting from free radical oxidation, type I photooxidation and peroxygenase-mediated oxidation of oleic acid.

(Table 3). Homolytic cleavage of hydroperoxides catalyzed by metal ions results in the formation of allylic peroxyl or alkoxyl radicals, while homolysis of the O—O bond by UVR affords alkoxyl radicals. Peroxyl radicals seem to play a key role in the allylic rearrangement of allylic hydroperoxides (Porter et al., 1995) (Fig. 6). Alkoxyl radicals thus formed can then: (i) abstract a hydrogen atom from another molecule to give hydroxyacids, (ii) lose a hydrogen atom to yield ketoacids, or (iii) undergo β-cleavage reaction affording volatile products. It may be noted that hydroxyacids and ketoacids may also result from disproportionation of two alkoxyl radicals (Fig. 6). Allylic ketoacids resulting from the degradation of hydroperoxides also absorb in the UVR range and may be excited to a triplet state, which can then: (i) undergo direct photodegradation reactions to volatile products or (ii) induce type I photosensitized processes. These compounds may also afford ω-oxocarboxylic acids and aldehydes after addition of water and retroaldolisation reaction (Fig. 6).

9,10-Epoxyoctadecanoic acid has been previously reported in marine (Stephanou, 1992) and urban (Stephanou and Statigakis, 1993) aerosols and found to be labile. Epoxyacids are in fact strongly degraded during the treatment; in addition to a partial reduction with $NaBH_4$ (Marchand and Rontani, 2001), they undergo alcoholysis and hydrolysis during alkaline hydrolysis and are converted to chlorohydrins and 9,10-dihydroxyacids during acidification (Holloway and Brown-Deas, 1973). We detected significant proportions of methoxyhydrins, diols and chlorohydrins resulting from the degradation of 9,10-epoxyoctadecanoic acid in the different samples investigated (Table 6). Epoxides may be formed by classical addition of a peroxyl radical to a double bond followed by fast intramolecular homolytic substitution (Fossey et al., 1995) (Fig. 4). However, this reaction becomes competitive (relative to allylic hydrogen atom abstraction) only in the case of conjugated, terminal, or trisubstituted double bonds (Schaich, 2005). In the case of oleic acid the formation of epoxide by autoxidative processes is thus very unlikely. The highest amounts of 9,10-epoxyoctadecanoic acid observed in the samples (12S2, 18S2 and 26S2) containing the highest proportions of allylic hydroperoxyacids (Table 6), led us to attribute the formation of this compound to the involvement of a peroxygenase (hydroperoxide-dependent oxygenase) during abiotic degradation of higher plant debris, fungi, yeasts or bacteria contained in aeolian particles. Such enzymes catalyzed epoxidation of unsaturated fatty acids in the presence of alkylhydroperoxides as co-substrates (Fig. 4) and play a protective role against the deleterious effects of fatty acid hydroperoxides *in vivo* (Blée and Schuber, 1990).

3.4.3. Sterols

Oxidation products deriving from source-specific lipids, such as Δ^5-sterols, convey useful information about the degradation state of lipids derived from specific organisms, usually when abundances

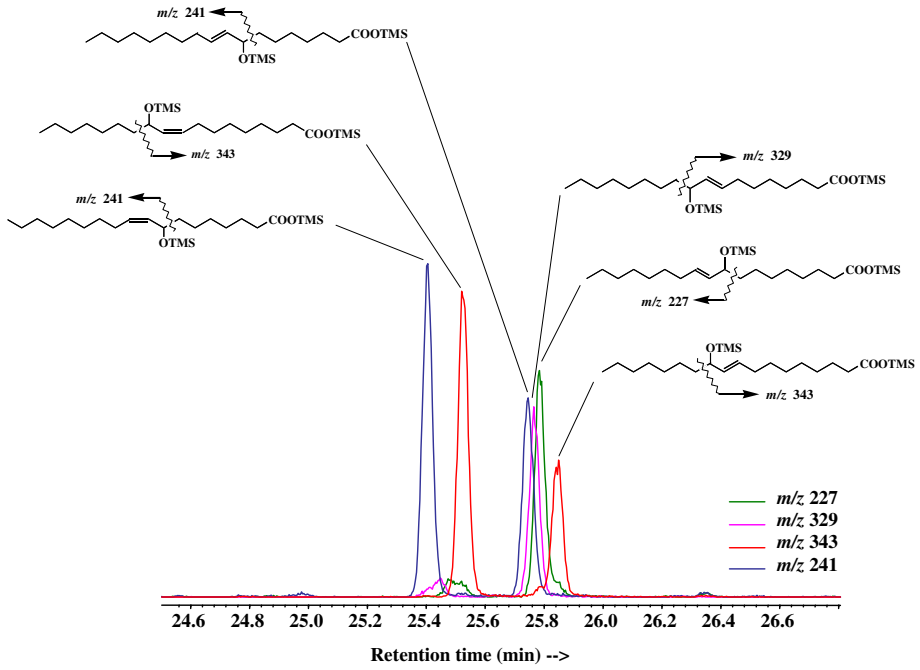

Fig. 5. Partial mass chromatograms of *m*/*z* 227, 241, 329 and 343 showing the presence of six isomeric allylic hydroxyacids deriving from oleic acid in the silylated reduced saponified fraction of the sample 12S2.

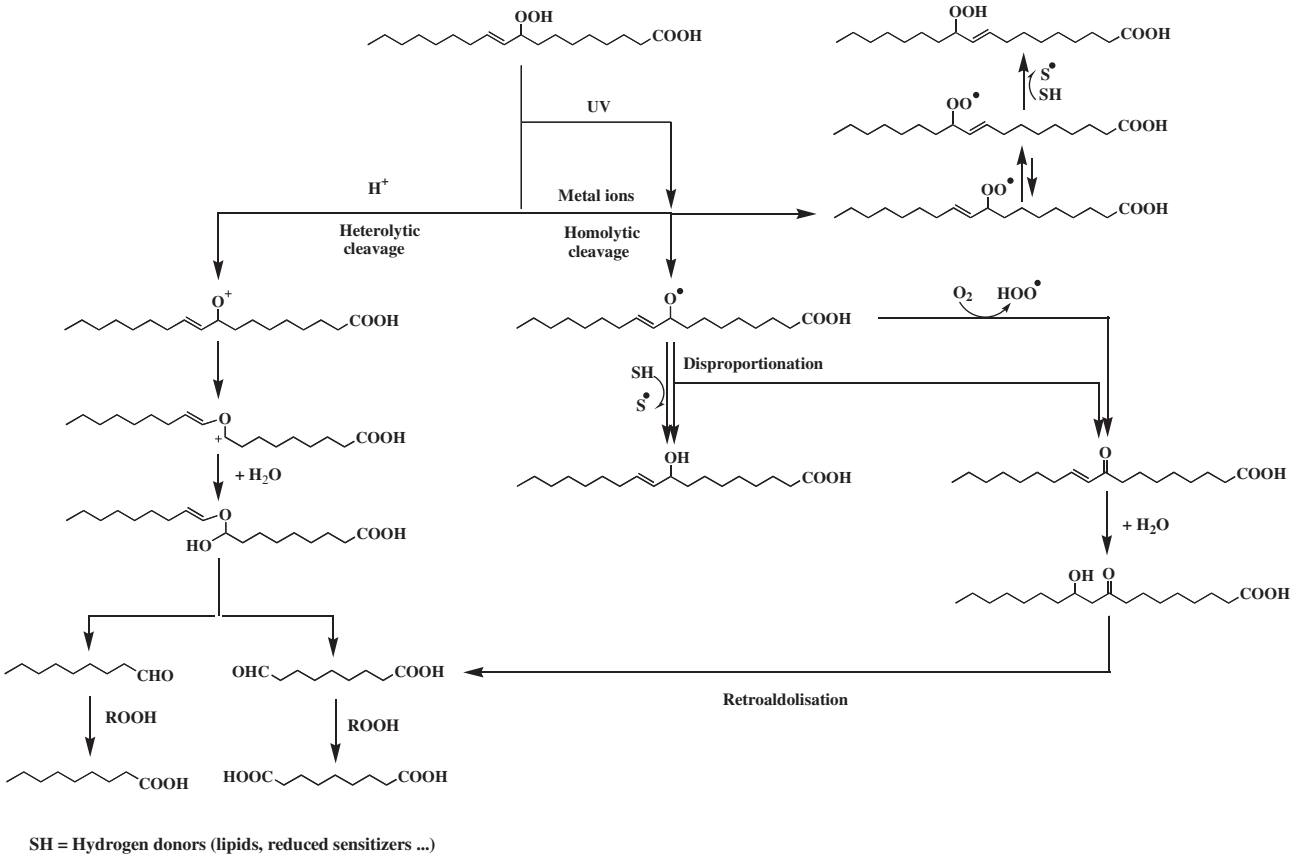

Fig. 6. Proposed pathways for the degradation of allylic hydroperoxyacids in aeolian particles (to simplify the scheme only the degradation of 9-hydroperoxyoctadec-10-enoic is shown).

are compared to the undegraded precursors. We tested the relative importance of biodegradation, photooxidation, and autoxidation for different components of aeolian particles by quantifying degradation products of three 'model' Δ^5-sterols: sitosterol and 24-methylcholest-5-en-3β-ol (campesterol) (both mainly arising from higher plants) and cholesterol (arising from meat cooking operations and other sources).

Aerobic bacteria may completely remineralize Δ^5-sterols (Naghibi et al., 2002), or they may sequentially convert Δ^5-stenols to ster-4-en-3-ones, 5α(H)-stan-3-ones and 5α(H)-stanols (Gagosian et al., 1982; Wakeham, 1989). These steroid ketones and stanols thus constitute useful indicators of bacterial degradation of sterols. During the treatment ($NaBH_4$ reduction and alkaline hydrolysis), ster-4-en-3-ones and 5α(H)-stanones were converted to ster-4-en-3-ols and 5α(H)-stanols, respectively (Fig. 7).

Free radical autoxidation of Δ^5-sterols yields mainly 7α- and 7β-hydroperoxides and, to a lesser extent, 5α/β,6α/β-epoxysterols and 3β,5α,6β-trihydroxysterols (Smith, 1981) (Fig. 7). Here, we selected 3β,5α,6β-trihydroxysterols as tracers of sterol autoxidation. 7-Hydroperoxides were discarded on the basis of their lack of specificity and their instability (Christodoulou et al., 2009) (Fig. 7) and 5α/β,6α/β-epoxysterols could not be used since they are converted to the corresponding triol during the saponification step we used. Sterol autoxidation percentage was estimated with the following equation: Sterol autoxidation % = (3β,5α,6β-trihydroxysterols %) x 2.4, on the basis of results from different incubation experiments and autoxidation rate constants previously calculated by Morrissey and Kiely (2006).

Singlet-oxygen mediated photooxidation (type II photoreactions) of Δ^5-sterols produces mainly Δ^6-5α-hydroperoxides with low amounts of Δ^4-6α/6β-hydroperoxides (Kulig and Smith, 1973) (Fig. 7). Δ^4-6α/6β-hydroperoxides were selected as tracers of photooxidation of Δ^5-sterols due to their high specificity and relative stability (Christodoulou et al., 2009; Rontani et al., 2009). These compounds were quantified after $NaBH_4$ reduction to the corresponding diols and the sterol photooxidation percentage

Table 7
Biotic and abiotic degradation of Δ^5-sterols in the different samples.

	7S2	8S2	9S2	10S2	12S2	18S2	26S2	36S2
Sitosterol								
Autoxidation percentage[a,b]	17.0	5.8	28.7	26.8	53.9	21.1	61.3	7.1
Type II photooxidation percentage[c]	23.2	19.2	26.0	23.6	24.9	14.5	49.3	6.9
Biodegradation product percentage[d]	4.4	3.9	5.1	5.5	2.0	0.9	5.9	3.7
Total degradation percentage	44.6	28.9	59.8	55.9	80.8	36.5	116.5	17.6
Campesterol								
Autoxidation percentage	17.6	5.7	19.4	36.6	53.2	20.3	68.4	25.2
Type II photooxidation percentage	21.5	19.0	17.7	37.9	23.1	24.8	52.0	nd
Biodegradation product percentage	8.4	13.5	6.7	6.1	2.5	1.7	17.3	12.7
Total degradation percentage	47.5	38.2	43.8	80.6	78.8	46.8	137.7	37.8
Cholesterol								
Autoxidation percentage	27.4	12.7	24.7	20.0	22.0	23.0	31.8	11.3
Type II photooxidation percentage	40.3	14.2	15.5	11.6	10.8	17.3	19.3	8.7
Biodegradation product percentage	8.0	7.1	5.9	4.9	20.3	32.4	48.8	13.5
Total degradation percentage	75.7	34.0	46.1	36.5	53.1	72.7	99.9	33.5

[a] Relative to the residual parent compound.
[b] Estimated with the equation: Sterol autoxidation % = (3β,5α,6β-trihydroxysterols %) × 2.4.
[c] Estimated with the equation: Sterol photooxidation % = (Δ^4-3β,6α/β-dihydroxysterol %) × (1 + 0.3)/0.3.
[d] Stanol %.

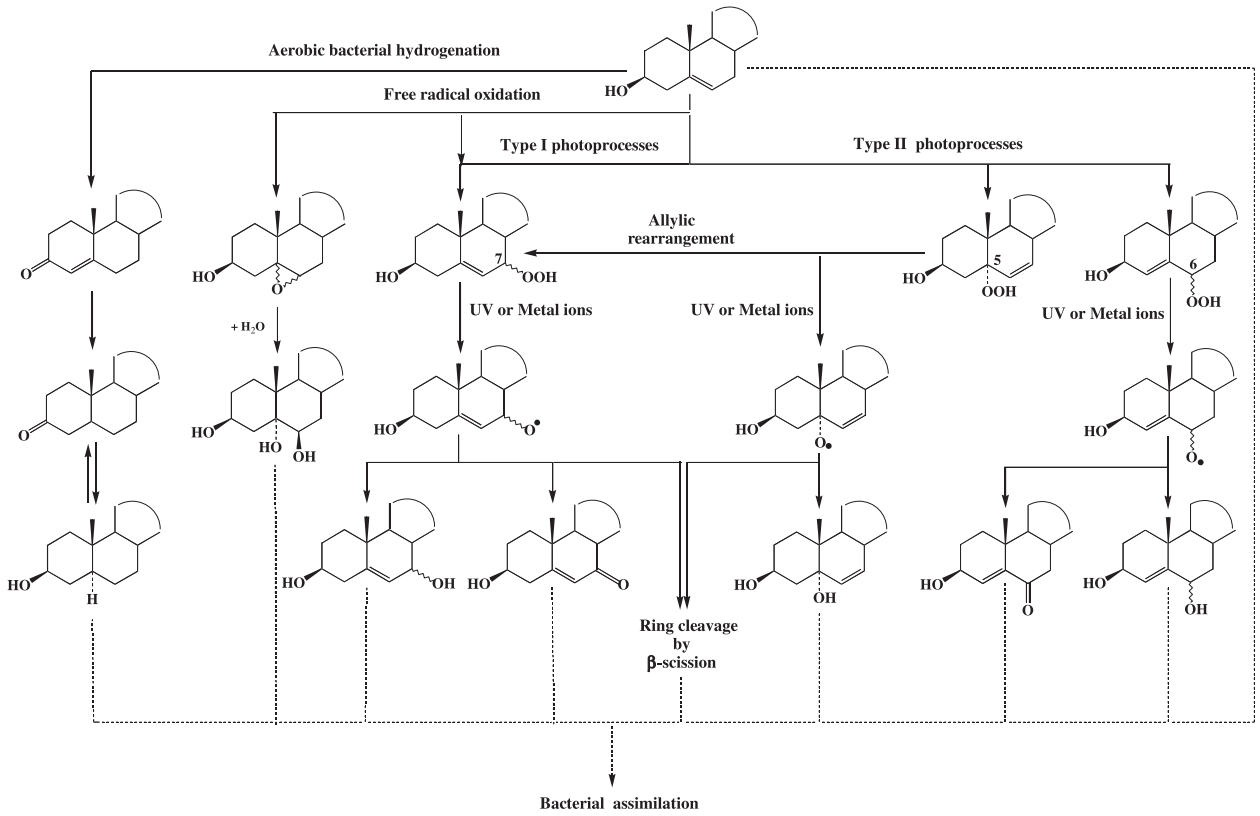

Fig. 7. Proposed pathways for the biotic and abiotic degradation of Δ^5-sterols.

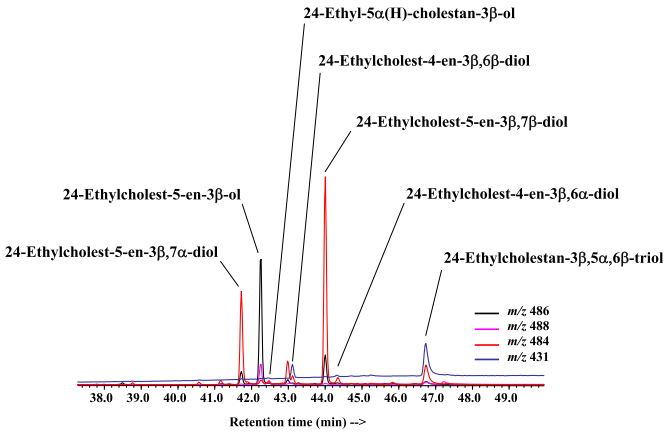

Fig. 8. Partial mass chromatograms of *m*/*z* 486, 488, 484 and 431 showing the presence of degradation products of sitosterol in the silylated reduced saponified fraction of the sample 12S2.

was estimated with the following equation (Christodoulou et al., 2009; Rontani et al., 2009): Sterol photooxidation % = (Δ^4-3β,6α/β-dihydroxysterol %) * (1 + 0.3)/0.3, based on the ratio Δ^4-6α/6β-hydroperoxides/Δ^6-5α-hydroperoxides measured in biological membranes (0.30, Korytowski et al., 1992).

Type I photosensitized oxidation of Δ^5-sterols mainly affords 7-hydroperoxides (Rontani et al., 1993) (Fig. 7). Unfortunately, these compounds are not sufficiently stable and specific (Fig. 7) to be used to estimate the importance of these degradation processes in aeolian particles.

The use of the proposed tracers to estimate the relative importance of the degradation processes requires the condition that the removal rates of these compounds (by further degradation) are similar to that of the parent Δ^5-sterol. Although each sterol and its degradation products may be potentially totally mineralized by marine bacteria, we assume that they should exhibit similar reactivity towards bacterial degradation (Rontani et al., 2009; Christodoulou et al., 2009).

The results of the quantification of degradation products of Δ^5-sterols are reported in Table 7. As in the case of oleic acid oxidation products (Table 6), the highest degradation of the three sterols was observed for the sample 26S2. Interestingly, the behaviour of phytosterols (sitosterol and campesterol) appeared to be well distinct from that of cholesterol. Indeed, degradation of the phytosterols mainly involved photo- and autoxidation processes (Fig. 8), while bacterial processes played an additional significant role in the degradation of cholesterol.

Type II photodegradation processes act intensively on lipid components of higher plants during the senescence (Rontani et al., 1996). On the basis of the lack of chlorophyll (singlet oxygen inducer sensitizer) in aeolian particles, the relatively high photooxidation state observed in the case of sitosterol and campesterol (except for the 36S2 sample) (Table 7) was attributed to intense photooxidation of senescent higher plants on land rather than to photooxidation of such material during aeolian transport. In higher plant debris, homolytic cleavage of photochemically produced hydroperoxides induced by metal ions (Schaich, 2005) and UV radiation (Christodoulou et al., 2010) may then initiate free radical oxidation of these two sterols during aeolian transport. The relatively weak autoxidation state of sitosterol and campesterol observed in samples 7S2 and 8S2 (Table 7) could result from the expected diatom contribution to these samples (see section 3.3.1). Indeed, it was previously observed that free radical oxidation processes act more strongly in higher plant debris than in phytoplanktonic cells (Rontani et al., 2011). Sterols associated with waxy vascular plant debris might be physically protected from enzymatic attack (Hedges and Keil, 1995), which could explain the relatively

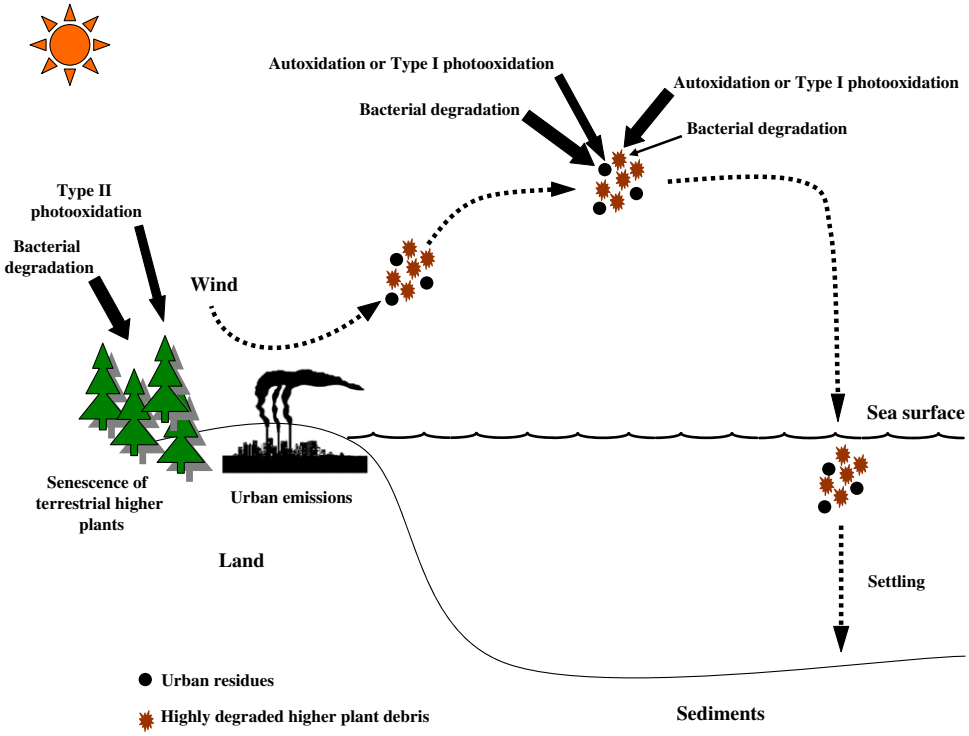

Fig. 9. Conceptual model showing the relative importance of photooxidation, autoxidation and bacterial biodegradation on land and in aeolian particles (thickness of arrows indicates relative importance of each degradative process).

weak biotic degradation observed in the case of sitosterol and campesterol (Table 7).

Cholesterol arising from meat cooking (and other sources) appears to be significantly affected by abiotic degradation processes in all the samples (Table 7). However, high proportions of 5α(H)-cholestan-3β-ol (cholestanol) (attesting to the involvement of intense biodegradation) were also observed in the samples 12S2, 18S2 and 26S2. Bacterial degradation acted intensively during the April–July period, i.e., when the temperature was highest. The increase of temperature during spring and summer likely favoured bacterial growth on the particles and thus biodegradation processes in these samples. The highest proportions of *cis*-vaccenic acid (a typical bacterial biomarker; Sicre et al., 1988) observed during this period (ratio $C_{18:1\omega7}/C_{16:0}$ ranging from 0.14 to 0.37 for the samples 12S2, 18S2 and 26S2 instead from 0.01 to 0.07 for the other samples) (Table 3) well support this hypothesis.

4. Conclusions

Eight samples of aeolian particles were collected on the Frioul Islands (north-western Mediterranean Sea) during 2010. Classical lipid biomarker analyses allowed to show a significant contribution of terrestrial higher plant debris to some of the samples. The presence of wind-blown fresh water diatoms in the samples 7S2 and 8S2 (collected in February–March) was suspected, while meat cooking residues seem to also contribute to some of the samples.

We used specific lipid degradation products that have been proposed for distinguishing biotic from abiotic processes (Rontani et al., 2009, 2011; Christodoulou et al., 2010), to estimate the roles played by heterotrophic, photodegradative, and autoxidative processes in the degradation of these particles. For a correct estimation, it was important to differentiate the degradation processes acting on land (in senescent higher plants and soils) from these really acting during aeolian transport. Labile degradation products of the non-specific oleic acid appeared to be very useful to estimate the effects of abiotic degradation processes on bulk OM during aeolian transport, while stable Δ^5-sterol degradation products give averaged information about the degradation of specific materials on land and during the transport.

By using these two kinds of tracers, we could estimate that the degradation of higher plants on land mainly involves type II (i.e., singlet oxygen involving) photooxidation during senescence and subsequent bacterial degradation processes in soils. Then, during aeolian transport, due to the lack of chlorophyll (singlet oxygen inducer sensitizer), higher plant debris mainly undergo autoxidation and/or Type I photooxidation processes and seem to be relatively well preserved (probably by cuticular waxes) towards bacterial degradation processes (Fig. 9). In contrast, bacteria play an important role in the degradation of the material arising from urban emissions (meat cooking) mainly during the spring-summer period.

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